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Deuterium Nuclear Magnetic Resonance of Phenol-d_5 in Nylon 6 under Active Uniaxial Deformation

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ABSTRACT: A stretching device suitable for fitting within a deuterium nuclear magnetic resonance (NMR) probe was constructed to investigate the large strain uniaxial tensile deformation behavior of nylon 6 plasticized by 40 wt % of phenol-d_5. The phenol-d_5 molecules probe the environment of the amorphous regions in nylon 6; the phenol-d_5 molecules do not exist in a "free" state, and they remain associated with the amide groups by hydrogen bonding during deformation. Deuterium NMR spectra show that the quadrupolar splitting varies linearly with strain throughout the experiment, indicating that the orientation of the phenol-d_5 molecules in the amorphous phase is simply a function of strain and not of stress. The line width increases with strain at low-to-moderate strains but attains a constant value at large strains (in the strain-hardening regime). From low-to-moderate strains, the line width behavior arises from a decrease in the translational motion of the phenol-d_5 molecules between amide groups in the amorphous chains during elastic deformation and during the transformation of the lamellar structure of nylon 6 to a fibrillar one. At large strains, the existence and deformation of the fibrillar structure cause the phenol-d_5 molecules to be confined to their respective amide groups on the time scale of the NMR measurement (~0.1 ms), resulting in a constant line width.

Introduction

Understanding the mechanisms of deformation in semicrystalline polymers is of primary importance in their design and improvement. The sequence of events occurring during elastic, intermediate and large strain plastic deformation has been treated in several papers.[1−3] There are many techniques which can probe the changes in the polymer as it is being deformed. Atomic force microscopy and wide- (WAXS) and small-angle X-ray spectroscopy (SAXS) have been used to obtain orientation and morphological information in both amorphous and crystalline regions.[4,5] Furthermore, information on molecular motions can be probed by nuclear magnetic resonance (NMR) techniques.[6,7] Most of these experiments, however, are usually performed on the polymer only after deformation has ceased, i.e., when the polymer is in a "dead" state. Thus they do not take into account the dynamics of the molecular chains when the polymer is in an active state of deformation. It would be interesting to directly observe any molecular motions or relaxations which may be activated during yield and cold drawing. Recently, Butler et al. have done time-resolved simultaneous X-ray of polyethylene undergoing active cold drawing to correlate the microscopic and macroscopic processes that occur during deformation.[8] Murty et al. employed NMR to evaluate strain-enhanced vacancy concentration in aluminum and ionic crystals which are deforming,[9,10] whereas Hansen et al. investigated the mobility of phenyl groups in polycarbonate by deuterium NMR during small strain deformation.[11] In this study, we use deuterium NMR to examine the behavior of deuterated phenol-d_5 in nylon 6 which is undergoing large strain deformation.

It is known that nylon can be plasticized by various molecules such as water, alcohols, acids, and phenols.[12] Plasticization reduces the Young's modulus and yield stress but increases the toughness of the material.[13−15] Andrews et al. have examined the effect of phenol absorption on the mechanical properties of nylon films.[16−19] Since phenol is a solid at room temperature, it is first dissolved in CCl_4 and nylon 6 is then put into the resulting solution. The phenol molecules penetrate into the amorphous regions of nylon 6. The use of phenol-d_5 (C_6D_5OH) gives high signal-to-noise spectra due to the 5 deuterons on each phenol molecule and due to its high equilibrium solubility (68 g phenol/100 g nylon 6 at 30 °C)[18] in nylon. Moreover, since the OH in phenol-d_5 is not deuterated, there will not be any exchange processes with the amide groups which would complicate the NMR spectra. Since the deformation behavior of a plasticized semicrystalline polymer is a complex process involving both the crystalline and amorphous chains, the phenol-d_5 molecules which are associated with the amorphous regions provide us with information regarding processes occurring in the amorphous phase.

Materials and Methods

Nylon 6 rods (2 mm diameter) were purchased from Goodfellow Corporation, and phenol-d_5 was obtained from Cambridge Isotope Laboratories. The molecular weight of the polyamide is 60 000, determined from viscometry measurements using 2,2,2-trifluoroethanol as a solvent at 23.5 ± 0.5 °C. Differential scanning calorimetry (DSC) showed that the crystallinity of the material is about 30%. Without any further modification, the rods were dried in a vacuum at 100 °C for 48 h to reduce the amount of trace water. The rods were then placed in a 0.25 M solution of phenol-d_5 in CCl_4 for about 2 days. The results of Addy and Anderson showed that nylon 6 preferentially absorbs the phenol molecules and that the amount of CCl_4 absorbed (about 2%) is negligible compared to that of phenol.[18] The mass of phenol-d_5 absorbed was determined by measuring the weight of the nylon 6 rod before and after immersion in the phenol-d_5/CCl_4 solution. Because 40 wt % of phenol-d_5 was absorbed, this indicates that the ratio of phenol-d_5 molecules to amide groups in the amorphous regions is approximately 1:1. These rods were then subsequently used in Instron and NMR experiments.

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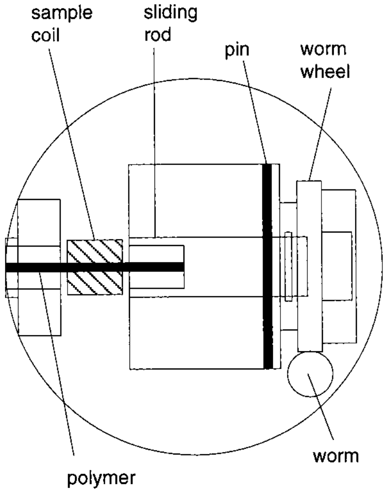

Figure 1. Schematics of the in situ stretching device in the deuterium NMR probe.

The uniaxial tensile experiment was performed on an Instron 4201 machine to obtain the stress−strain curve. The gauge length of the sample was 10 mm, and it was stretched to 20 mm at an elongation rate of 0.25 mm/min. Over the 40 min time scale of the experiment, there was negligible loss of phenol-d_5 molecules to the atmosphere.

The deuterium NMR probe was modified to perform in situ uniaxial tensile experiments. Figure 1 shows the schematics of the probehead with the stretching device. One end of the polymer sample was held by a stationary support, and the other end was attached to a sliding rod. The sliding rod was set in motion by a worm and worm gear assembly, which was in turn driven by a motor located outside the magnet. This mechanical stretching device is akin to a miniature Instron machine, and the tensile experiment was repeated in the probe while NMR acquisition was simultaneously performed.

The NMR work was done at room temperature of approximately 22 °C (since there is no temperature control as on liquids NMR spectrometers) at 45.8 MHz for deuterium. The 90° pulse time was 5.4 μs. Free induction decays (FID) were obtained by using a single 90° pulse. The digitization rate used was 1 μs with a total acquisition time of 2048 μs. The recycle delay was 0.1 s, and 1200 scans were needed for each spectrum.

Results and Discussion

Figure 2a shows the plot of engineering stress versus engineering strain (strain, ϵ, is defined as $\epsilon = \Delta L/L_0$ where ΔL is the increase in length and L_0 is the initial length of the sample) of nylon 6 which has gained 40 wt % of phenol-d_5. The curve shows a yield point, yield drop, and strain hardening. The deformation was homogeneous, and necking did not occur. The yield strength of 17 MPa is much lower than that of dry nylon (76 MPa),[15] indicating extensive plasticization of the nylon 6 rod by the phenol-d_5 molecules.

Figure 3 shows a series of deuterium NMR spectra of the phenol-d_5 molecules in the amorphous phase of the plasticized nylon 6 as a function of strain. The bottommost spectrum shows the spectrum of phenol-d_5 in undeformed nylon 6. It is a narrow Lorentzian with a line width of 1990 Hz, indicating that the order parameter is zero and that the phenol-d_5 molecules in the amorphous regions undergo fast isotropic reorientation compared to the quadrupolar interaction (~200 kHz). The line widths of the spectra increase with strain and eventually split into a doublet at higher strains. The sample in the probe deformed in a homogeneous manner without necking as in the corresponding Instron experiment.

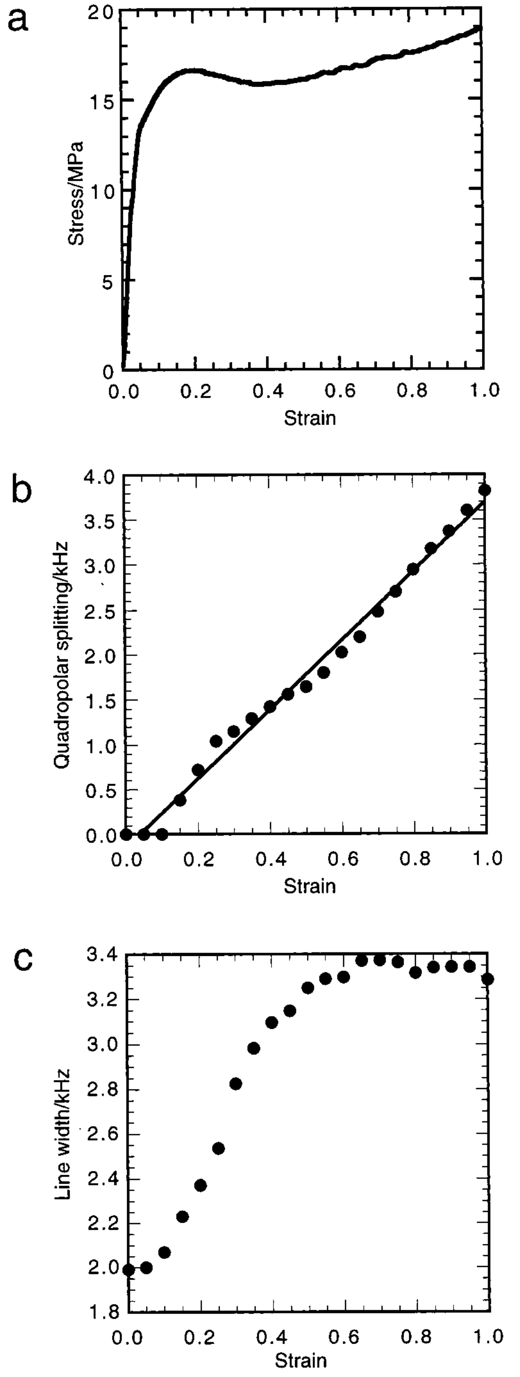

Figure 2. (a) Stress−strain curve of nylon 6 rod plasticized with phenol-d_5. The elongation rate is 0.25 mm/min. (b) Quadrupolar splitting/kHz versus strain. (c) Line width/kHz versus strain.

To confirm that the deformation occurring in the probe was indeed homogeneous, the inverse of the area under each spectrum was plotted against strain as shown in Figure 4. A straight line was obtained. Assuming that volume was conserved during the deformation process, the area under the NMR spectrum should follow the relationship

$$^{1}/_{A} \propto {}^{1}/_{V} = C_1\epsilon + C_2 \qquad (1)$$

where A is the area of the spectrum, V is the volume of

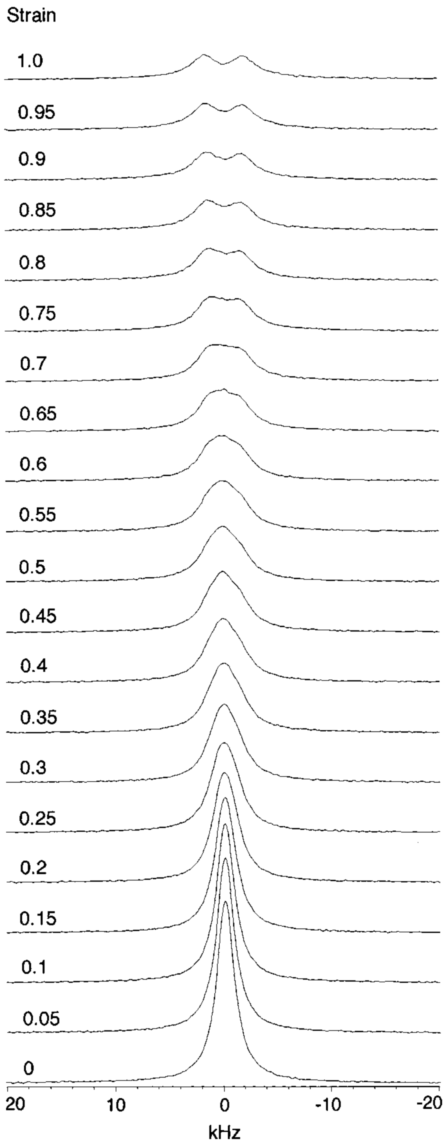

Figure 3. Deuterium NMR spectra of phenol-d_5 in nylon 6 rod undergoing active tensile deformation. The corresponding strains are shown on the left. The elongation rate is 0.25 mm/min. Each spectrum is the accumulation of 1200 scans with a digitization rate of 1 μs.

material within the NMR coil, ϵ is the strain,and C_1 and C_2 are constants which depend on the elongation rate and the dimensions of the coil and undeformed sample. Since eq 1 also shows a linear relation between the inverse of spectral area and strain, the deformation of plasticized nylon 6 occurring in the probe was homogeneous.

Figure 3 shows that, even at large strains, the spectra are still motionally narrowed with the appearance of a doublet. The NMR spectrum of a deuteron in a small molecule diffusing in an anisotropically ordered medium consists of a doublet whose splitting $\Delta\nu$ is given by[20−23]

$$\Delta\nu = {}^{3}/_{2}\nu_{q}[\langle P_2(\cos\theta)\rangle + {}^{1}/_{2}\eta\langle\sin^2\theta\cos 2\phi\rangle]P_2(\cos\Omega) \qquad (2)$$

where ν_q is the quadrupolar coupling constant, η is the asymmetry parameter, θ and ϕ are the instantaneous polar and azimuthal angles, respectively, between the CD bond and the stretching direction, and Ω is the angle between the stretching direction and the magnetic field.

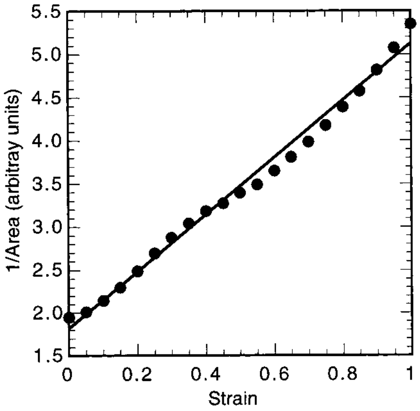

Figure 4. Inverse of the area of the deuterium NMR spectra in Figure 3 versus strain.

The quadrupolar splitting is directly related to the average order parameter $\langle P_2(\cos\theta)\rangle = \langle(3\cos^2\theta - 1)/2\rangle$ of the CD bonds of the phenol-d_5 molecules in the amorphous phase. The presence of a doublet in the spectra in Figure 3, then, indicates that phenol-d_5 molecules probing the amorphous regions have a nonzero order parameter. In those spectra showing a doublet, no central peak is observed. Thus, there are no “free” (i.e., isotropically mobile as in a liquid, thereby resulting in a narrow central Lorentzian peak[22,24]) phenol-d_5 molecules throughout the deformation process. Such a splitting has also been observed for benzene-d_6 in polystyrene solution of concentration of 125 mg/mL undergoing shear.[25]

As further proof of the anisotropy of the environment probed by the phenol-d_5 molecules due to deformation, the polymer was removed from the probe after the deformation. The sample contracted as it was released from stress. A section of the deformed specimen was cut and placed in the probe. NMR acquisition was done with the sample axis oriented at angles of $\Omega = 0°$ and $\Omega = 90°$ to the magnetic field. The resulting spectra are shown in Figures 5b and 5c. Table 1 shows the quadrupolar splittings and line widths for each of the spectra in Figure 5. When the sample is still under stress at maximum elongation (Figure 5a), the quadrupolar splitting and line width are 3860 and 3270 Hz respectively. The effects of the sample being released from stress can be seen by the reduced quadrupolar splitting (2160 Hz) and line width (2510 Hz) in Figure 5b. As expected from eq 2, the spectra for the relaxed specimen ($\Omega = 0°$) in Figure 5c shows twice the quadrupolar splitting (4240 Hz) compared to that in Figure 5b, indicating that the phenol-d_5 molecules are experiencing an anisotropic environment in the deformed material.

Each spectrum in Figure 3 was then regressed using two Lorentzian components, as shown in Figure 6. The distance between the peaks of the two components is taken to be the quadrupolar splitting. As the quadrupolar coupling constants and asymmetry parameters for the ortho/meta CD groups and the single para CD group are similar[26] and since the experimentally obtained narrow Lorentzian line shapes are indicative of rapid motional averaging of the phenol-d_5 molecules relative to the quadrupolar coupling constant (∼200 kHz), it is assumed that the splitting arising from para CD bonds is similar to that from the ortho/meta CD bonds. Thus, we have not attempted to fit the spectra in Figure 3 with four Lorentzian components. Figures 2b and 2c show, respectively, the variation of the quadrupolar splitting

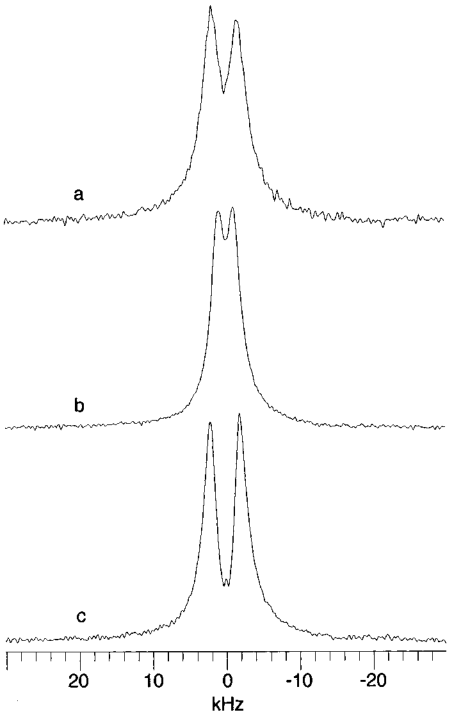

Figure 5. Deuterium NMR spectra of phenol-d_5 in nylon 6 rod with its axis at angles of $\Omega = 0°$ and 90° to the magnetic field: (a) at maximum elongation under tension with $\Omega = 90°$, (b) after release from tension with $\Omega = 90°$, and (c) after release from tension with $\Omega = 0°$.

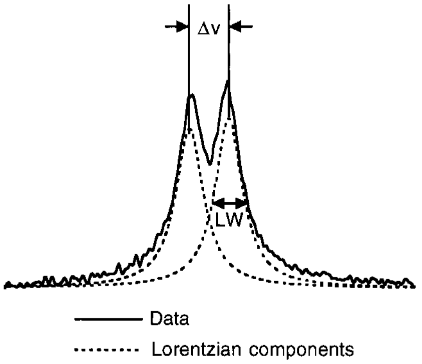

Figure 6. Deuterium spectrum in Figure 3 at a strain of 0.85, with the least-squares components obtained by regression. The quadrupolar splitting is represented by $\Delta\nu$ and the line width by LW.

Table 1. Quadrupolar Splittings and Line Widths of Spectra in Figure 5

spectrum in Figure 5	quadrupolar splitting/Hz	line width/Hz
5a	3860	3270
5b	2160	2510
5c	4240	2170

and line width (taken as the average of the line widths of the two fitting components) with strain.

From Figure 2b, the splitting varies fairly linearly (as shown by the straight line drawn through the data points) with strain even though the stress−strain curve shows nonlinear behavior. The splitting shows little deviation from linearity at strains where yield, yield drop, and strain hardening are observed. This indicates that the orientation of the phenol-d_5 molecules associated with the amorphous chains is a function of strain rather than of stress.

On the other hand, the line width data in Figure 2c behaves differently. At low and intermediate strains, the increase in line width with increasing strain indicates that the mobility of the phenol-d_5 molecules in the amorphous phase decreases as the polymer is being elongated. At a strain of 0.6 and higher, the line width is invariant with strain.

The hydroxyl group of phenol is hydrogen-bonded to the carbonyl oxygen of nylon 6 in the amorphous regions.[19] However, the observation of the narrow Lorentzian line shapes proves that the presence of hydrogen bonding does not constrain the motion of a phenol-d_5 molecule at the amide site to a large degree since the line shapes correspond to fast isotropic reorientation rather than rapid continuous diffusion about the ring axis or two-site 180° jumps.[27] Furthermore, translational diffusion of phenol-d_5 from one amide site to another as occurs for D_2O cannot be ruled out.[28]

At small strains, the increase in quadrupolar splitting[29] reflects the order of the phenol-d_5 molecules associated with the orientation of the amorphous chains as a result of interlamellar shear and other processes that tend to align these chains in the draw direction. The phenol-d_5 molecules are sampling a more anisotropic environment which restricts their motion, thereby resulting in an increase in line width of the spectra. At the yield point, crystallographic slip of the nylon 6 crystals occurs to relieve the stresses on the tie molecules, followed by transformation of the lamellar structure of the crystalline regions to a fibrillar structure during strain softening. The overall effect is to allow the amorphous chains to attain a higher degree of orientation, thereby increasing the quadrupolar splitting and line width of the phenol-d_5 spectra.

The subsequent load-extension curve plateau and strain hardening result from the deformation of the fibrillar structure. Though the quadrupolar splitting continues to increase in this region, the line width reaches a constant value after a strain of about 0.6, which corresponds to the onset of strain hardening in the stress−strain curve. As before, the increase in splitting is attributed to an increase in the orientation of the phenol-d_5 molecules directly probing the structural rearrangements of the chains in the amorphous phase as they continue to align along the tensile axis due to deformation. The results of Galeski et al. show that the amorphous phase of water-plasticized nylon 6 is able to undergo large plastic deformation without cavitation.[15] Thus, the cessation of the increase in line width is not due to void formation allowing more degrees of freedom for the phenol molecules. It would then appear that once the fibrillar structure is formed, the environment probed by the phenol molecules does not change much even though the chains in the amorphous regions are attaining a higher degree of orientation.

To obtain a better physical picture of the dynamics of the phenol-d_5 molecules during deformation, spin−lattice (T_1) relaxation experiments were performed for undeformed nylon 6 rods which had absorbed different amounts of phenol-d_5. The behavior of phenol-d_5 in nylon 6 can be modeled as both translational reorientation between amide sites and rotational reorientation within individual amide sites, similar to that of D_2O in nylon 6.[28] For a spin 1 quadrupole with zero asymmetry parameter, the longitudinal (T_1) and transverse (T_2) relaxation times are related to the spectral densities by

$$\frac{1}{T_1} = \frac{3\pi^2}{20}\nu_q^2\{J_1(\omega_0) + 4J_2(2\omega_0)\} \tag{3}$$

$$\frac{1}{T_2} = \frac{3\pi^2}{40}\nu_q^2\{3J_0(0) + 5J_1(\omega_0) + 2J_2(2\omega_0)\} \tag{4}$$

where ω_0 is the Larmor frequency of the deuteron, ν_q is the quadrupolar coupling constant of the CD bond, and J_0, J_1, and J_2 are the spectral densities. Due to the short T_1 and T_2 time constants of the samples, spin−echo experiments could not be used to measure T_2 directly. The value of T_2* was taken to be equal to T_2 as field inhomogeniety effects are small. T_2* is then obtained from the line widths of the spectra using the following equation:

$$\frac{1}{T_2^*} = \pi(\text{line width}) \tag{5}$$

If the solvent molecules undergo isotropic reorientation with correlation time τ_C, the spectral densities take on the following forms:

$$J_0 = \tau_c \tag{6}$$

$$J_1 = \frac{\tau_c}{1 + \omega_0^2\tau_c^2} \tag{7}$$

$$J_2 = \frac{\tau_c}{1 + (2\omega_0)^2\tau_c^2} \tag{8}$$

However, as in the case of D_2O in nylon 6,[28] assuming one correlation time alone causes a discrepancy between the T_1 and T_2* results, and eq 6 was modified to take into account an additional correlation time τ_T due to translational diffusion:[30,31]

$$J_0 = 2\tau_c + 4\epsilon^2\tau_T \tag{9}$$

where ϵ^2 is the mean square fractional change in the quadrupolar coupling and is assumed to be 1%.[31] The dependence of T_1 on the amount of phenol-d_5 absorbed by nylon 6 shows a minimum, indicating correlation times on the order of $\omega_0\tau_c \approx 1$. At the same time, the T_1 data could be fitted well with an exponential decay with only one time constant, indicating that there is only one distinct local environment for phenol-d_5 in the nylon matrix. For the sample used in the deformation experiment, the rotational (τ_C) and translational (τ_T) reorientation correlation times of phenol-d_5 were found to be 3.77 ns and 0.16 ms, respectively. An estimate can now be made for the diffusion coefficient, D, using the equation

$$D = \frac{L^2}{\tau_T}$$

where L is taken to be 8.70 Å, which is the distance between consecutive NH groups along a single nylon 6 chain in the α crystal phase[32] and represents an upper limit in the amorphous region. The resulting value for D is 4.75×10^{-11} cm^2/s, which is similar to that found for water in nylon 6.[33]

When the sample is deforming, either or both correlation times should change as the phenol-d_5 molecules experience different environments due to structural changes in the polymer. Since the spin−spin relaxation time, T_2, and hence line width are sensitive to slow motions,[30] we attribute the behavior of the line width with strain in Figure 2c to changes in the translational correlation time while the rotational correlation time remains unchanged. In the undeformed sample, the FID time scale of 0.16 ms is similar to that of τ_T. Therefore, one phenol-d_5 molecule makes an average of one hop between amide sites during the FID. Relaxation time analysis showed that the frequency of such hops is halved at high strains. We conclude that as the polymer is deformed at low and moderate strains, the frequency of the hops decreases, causing a corresponding increase in the line width. Because the translational correlation time constant τ_T increases with the line width,[28] these observations show that the diffusion coefficient decreases with increasing deformation. At high strains, the formation of a fibrillar structure in the polymer causes the probe molecules to remain (on the NMR time scale) at their respective amide sites, resulting in negligible further change in the line width of the spectra at strains greater than 0.6.

Conclusion

We have demonstrated the feasibility of performing simultaneous deuterium NMR experiment during the large strain tensile deformation of nylon 6 plasticized by phenol-d_5. The phenol-d_5 molecules probe the environment of the amorphous phase, do not exist in a free state, and are associated with the amide groups during deformation. The quadrupolar splitting varies linearly with strain. Thus, the order parameter of the phenol-d_5 molecules associated with chains in the amorphous regions is simply a function of strain and not of stress. The line width of the phenol-d_5 spectra increases with strain at low-to-moderate strain but attains a constant value at large strains in the strain-hardening regime. This is attributed to the decrease in the frequency of hops of the phenol-d_5 molecules between amide sites at low and moderate strains, until at high strains the formation of a fibrillar structure results in the phenol-d_5 molecules being confined to individual amide sites on the NMR time scale so that the line width no longer changes.

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